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Synthesis of a novel functional polymer immobilized platinum complex and its application in the catalytic hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane

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ABSTRACT

A novel polymer has been synthesized using 2-vinylpyridine as a functional monomer and allyl polyethylene glycol as a cross-linking agent, and platinum has been immobilized on this synthesized polymer. The resulting immobilized catalyst showed superior catalytic performance for the hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane as compared to homogenous platinum catalyst, polystyrene-immobilized platinum or other hydrosilylation catalysts. The conversion of silane is about 100% and the maximum yield of β-adduct is 92.3% with slightly α-adduct. Furthermore, the catalyst showed sufficient stability that it could be reused three times without noticeable inactivation.

1. Introduction

Fluoroalkylsilanes are interesting compounds due to their chemical and thermal stabilities and their surface activity [1–3]. The synthesis of precursors of fluorinated silicones requires the introduction of fluorinated groups on an Si atom, and this can be achieved either through an organometallic route [4,5] or by the hydrosilylation of fluorinated olefins or dienes under UV irradiation or in the presence of activating agents such as peroxides or catalysts based on multi-coordinated transition metal complexes [6–11].

Hydrosilylation is one of the most important reactions for the synthesis of functionalized silanes and polysiloxanes [12,13]. Generally, the hydrosilylation of olefins can be suitably performed in the liquid phase using a homogeneous catalyst, such as chloroplatinic acid (H_2PtCl_6), especially Speier's catalyst (a solution of H_2PtCl_6 in isopropyl) or Karstedt's catalyst (complex obtained by reaction of 1,3-divinyltetra-methyldisiloxane with H_2PtCl_6) [14]. However, attaining a good yield of the β-adduct and inhibiting secondary reactions is still a challenge. To this end, many research groups have focused on heterogeneous catalysts for hydrosilylation, and have reached many interesting conclusions [15,16]. Some organic polymer immobilized platinum catalysts have been used to catalyze the hydrosilylation, which showed excellent catalytic performance for specific substrates [17–20].

In this paper, we report a novel heterogeneous catalyst for the hydrosilylation of fluorinated olefins. This catalyst has been prepared by immobilized platinum on a novel functional styrene-based polymer. The catalytic properties of this catalyst with regard to the hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane (Scheme 1) have been investigated.

2. Results and discussion

2.1. Preparation and characterization of polymers functionalized with polyethylene glycol and pyridine groups

Polymers functionalized with polyethylene glycol and pyridine groups were prepared by the solvent free-radical polymerization of styrene with allyl polyethylene glycol as cross-linker and AIBN as initiator (Schemes 2 and 3).

The prepared polymer were designed as P1, P2, P3, P4, P5, P6, P7, P8, and C9, respectively. The polymers could be readily precipitated in polar solvents, and so it was easy to obtain polymer particles in powder form by simple precipitation from methanol. The yields of these products were as high as 80%. GPC with reference to a calibration curve based on low-polydispersity polystyrene standards showed that the molecular weight characterizations of all products exhibited prominent monomodal Gaussian distributions with comparable degrees of polymerization. For P2–P9, the polymers were prepared with the same ratio of cross-linking agent. The polymer dispersity indices of these products were above 1.5, in line with expectation for this kind of thermally initiated free-radical polymerization. The

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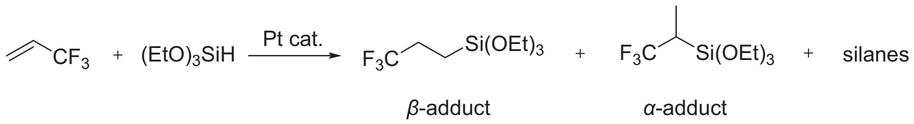


Scheme 1. Hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane.

polymerizations were carried out with the same free-radical initiator, styrene monomer, cross-linking agent, and solvent; only the 2-vinylpyridine content was varied. The molecular weight distributions in terms of M_n and M_w values proved to be similar for the different products, as indicated in Table 1.

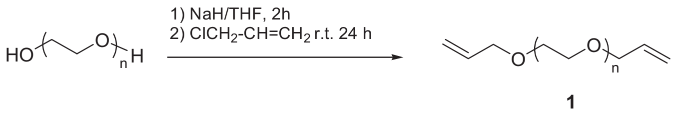
The contents of various elements in the polymers are listed in Table 2. Based on ICP trace element analysis, the carbon, hydrogen, nitrogen, and oxygen contents are in accordance with the prepared comonomer mixtures. From the elemental analysis data, it is evident that the copolymerization of styrene with 2-vinylpyridine had been successfully accomplished.

Corresponding catalysts were synthesized and designated as C1, C2, C3, C4, C5, C6, C7, C8, and C9, respectively. These catalysts were characterized by elemental analysis and atomic absorption spectroscopy (Table 3). All these catalysts are used in hydrosilyaltion to test their activities.

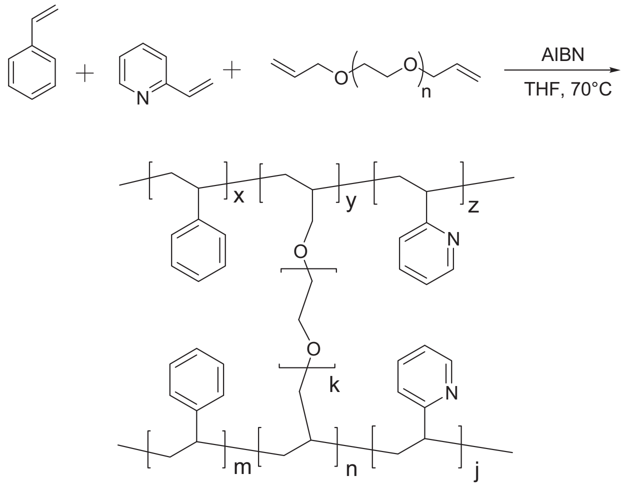
X-ray photoelectron spectroscopy (XPS) was used to further characterize the most excellent catalyst. The XPS data for polymer-Pt, polymer and $PtCl_4$ are listed in Table 3. It can be seen that the binding energies O_{1s} and C_{1s} of polymer-Pt are similar to those of polymer. However, the difference of N_{1s} binding energies between polymer-Pt and PS is 0.8 eV. The difference of Pt 4f binding energies between polymer-Pt and $PtCl_4$ is 0.3 eV. These results indicate that the coordination bond is formed between platinum and nitrogen atom in the complex (see Table 4).

2.2. Hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane

We proceeded to examine the hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane as catalyzed by the novel catalyst of platinum immobilized on polystyrene functionalized with polyethylene glycol and pyridine groups. For comparison, Speier's catalyst, Karstedt's catalyst, and a polystyrene (P1)-immobilized platinum catalyst were also used under similar reaction conditions. The results are presented in Fig. 1.



Scheme 2. Synthesis procedure of allyl polyethylene glycol.



Scheme 3. The structural representation of the novel polymer.

From Fig. 1, it can be seen that the conversion of triethoxysilane was 97.3% and the yield of β-adduct was 57.4% when Speier's catalyst (S1) was used. When Karstedt's catalyst (K1) was used for the reaction, the conversion was 94.1% and the yield of β-adduct was raised to 70.8%. Under the same conditions, a 79.7% yield of β-adduct was attained using the simple polymer (P1)-immobilized platinum. However, the yields of β-adduct achieved by using catalysts composed of platinum immobilized on the polymers incorporating allyl polyethylene glycol and pyridine groups exceeded those with the former three catalysts. It is worthy of note here that the incorporation of 2-vinylpyridine into the polymer and the subsequent immobilizing of the platinum complex increased the selectivity of β-adduct in comparison with the unfunctionalized polymer. The effect of the pyridine group on the reaction is pronounced. Initially, the yield of the β-adduct increased with the 2-vinylpyridine content. However, a notable decrease in catalytic activity was observed on further increasing the 2-vinylpyridine content in the copolymer. It is speculated that the electronic effect of the nitrogen of the pyridine group influences the electron cloud around the platinum atom and promotes the transformation of the Pt^{4+} and the Pt^{2+} valence state recycling. However, superfluous pyridine nitrogen decreases the catalytic activity owing to its strong complexing ability. The oxygen of the polyethylene glycol also contributes to adjusting the activity of the catalyst for the hydrosilylation reaction. This is evident from the fact that, for polymers with similar N/Pt atom ratios, the platinum catalyst immobilized on the polymer incorporating polyethylene glycol as the cross-linking agent gave a 92.5% yield, in contrast to the 79.7% yield with unfunctionalized polystyrene as the catalyst support. From the above results, we speculate that the existence of polyethylene glycol link make the platinum catalyst more active due to the electron-withdrawing ability of oxygen atom. This is in favor to form the circle between Pt^{2+} and Pt^{4+}. Additionally, on the basis of Chalk–Harrod mechanism for hydrosilylation, it is a crucial step that hydrogen atom add to the carbon atom of unsaturated compound. As a result of steric effect of $[OCH_2CH_2]_n$, hydrogen atom of Si–H added on the alpha carbon atom and beta carbon atom of trifluoropropyl to Pt atom. This reaction mode can make trifluoropropyl group keep away from the bigger complex platinum for reducing nonbonding interaction each other and pull down the energy of the whole system. At last, β-adduct as major product was attained with minor α-adduct, even not detect it.

We examined the hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane catalyzed with four catalysts (S1-Speier's catalyst, K1-Karstedt's catalyst, C1, and C6), and the results are presented in Fig. 2. A visible induction phase was apparent in the reactions promoted by the simple polystyrene-immobilized platinum catalyst, the novel catalyst, and Speier's catalyst. On the other hand, no remarkable induction period was observed in the hydrosilylation promoted by Karstedt's catalyst, which may be because of the very active Pt^0 state in this complex. When the hydrosilylation was carried out with Speier's catalyst or Karstedt's catalyst, a large number of by-products tetraethoxysilane and other silanes were generated. Under the same conditions, the yield

Table 1
Characterization of polymers synthesized.

Polymer	Comonomer mixture (g)			Polymerization yield (%)	M_n	M_w	PDI
	St	APEG	2-VPy				
P1	2.1	–[a]	0.20	86.9	10056	25437	2.53
P2	2.1	0.06	0	82.1	6642	11897	1.79
P3	2.1	0.06	0.05	81.8	6488	10999	1.70
P4	2.1	0.06	0.10	80.3	7660	12756	1.67
P5	2.1	0.06	0.15	83.4	7075	12946	1.83
P6	2.1	0.06	0.20	82.7	6376	10466	1.64
P7	2.1	0.06	0.25	81.6	6814	11429	1.68
P8	2.1	0.06	0.30	80.9	7388	12556	1.70
P9	2.1	0.06	0.5	81.7	9808	16709	1.70

St = styrene; APEG = allyl polyethylene glycol; 2-VPy = 2-vinylpyridine; M_n = the number average of relative molecular weight; M_w = the weight average of relative molecular weight; PDI = M_w/M_n (polydispersity).

[a] Replace of APEG with equivalent divinylbenzene.

Table 2
Composition of precursor polymer.

Precursor	Theoretical composition/%				Experimental result/%			
	C	H	O	N	C	H	O	N
P1	91.15	7.69	–	1.14	90.27	8.42	–	0.98
P2	91.42	7.76	0.81	–	90.31	8.27	0.51	–
P3	91.16	7.74	0.79	0.30	90.78	7.78	0.51	0.23
P4	90.91	7.73	0.77	0.59	90.65	7.79	0.52	0.54
P5	90.67	7.69	0.76	0.86	90.24	7.68	0.53	0.75
P6	90.44	7.67	0.74	1.13	90.10	7.62	0.56	0.89
P7	90.22	7.65	0.73	1.38	89.91	7.62	0.57	1.12
P8	90.00	7.63	0.71	1.62	89.69	7.60	0.56	1.42
P9	89.24	7.56	0.66	2.50	88.89	7.50	0.54	2.24

Table 3
Composition of catalysts.

Catalysts	C1	C2	C3	C4	C5	C6	C7	C8	C9
Pt (wt %)[a]	1.79	1.82	1.90	1.84	1.91	1.88	1.93	1.98	1.97
N/Pt(mol)	6.7	–	1.5	3.7	5.1	6.1	7.8	9.6	14.6
O/Pt(mol)	–	2.9	3.3	3.3	3.2	3.3	3.2	3.1	3.0

[a] The content of platinum of catalysts by atomic absorption spectroscopy.

of this by-product decreased when using simple polystyrene-immobilized platinum. Using catalyst C6, the yield of tetraethoxysilane was very low, so that the yield of adduct was increased up to 92.5%. It was noted that the reaction mixture containing the catalyst C6 was colorless, whereas yellow reaction mixtures were obtained when using S1 or K1, suggesting that colloidal platinum of the homogeneous catalysts could be dissolved in the reaction mixture. Moreover, some platinum will usually be reduced to platinum black, which shows no activity for hydrosilylation. On the contrary, this phenomenon did not arise with the novel polymer-immobilized platinum catalyst.

Furthermore, the catalyst C6 could be reused three times. The conversion of triethoxysilane was above 90% and the yield of the β-adduct was about 80%. The results were listed in Fig. 3. However, both conversion and yield decrease varying degrees. It is possible reason that a small quantity of platinum leach from polymer

Table 4
XPS data for PS-Pt, PS and $PtCl_4$.

Sample	$Pt_{4f7/2}$	N_{1s}	O_{1s}	C_{1s}
PS-Pt	75.2	402.2	535.0	286.6
PS		401.4	535.0	286.6
$PtCl_4$	75.5			

The binding energies are referenced to C_{1s} (284.6 eV).

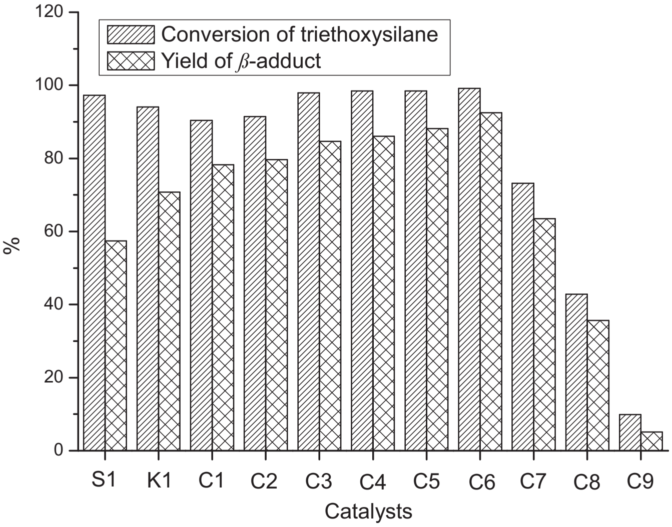


Fig. 1. Conversion of triethoxysilane and yield of β-adduct in the reaction by various catalysts
S1-Speier's catalyst, K1-Karstedt's catalyst. Reaction condition: 60 °C, 8 h.

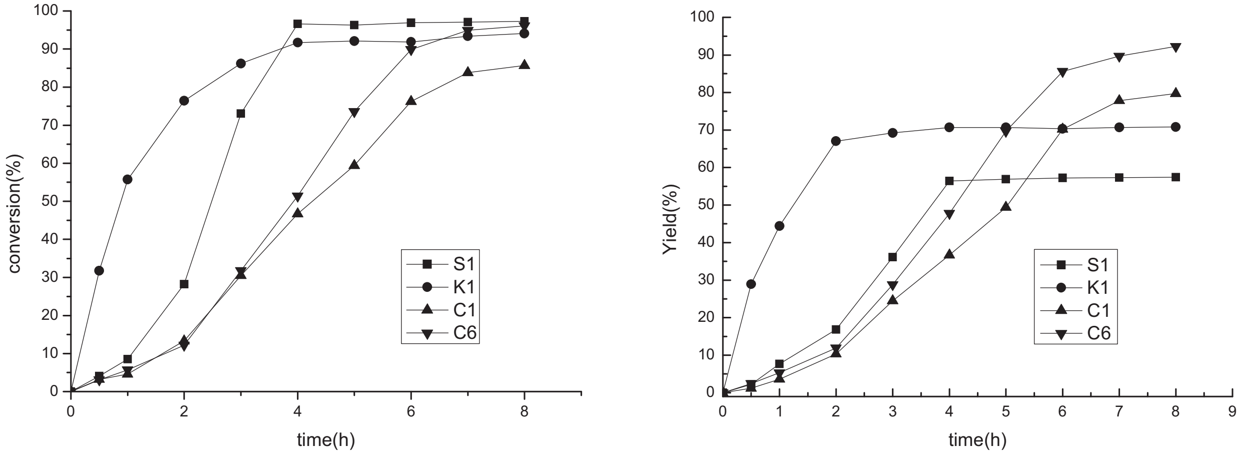


Fig. 2. Conversion and yield versus reaction time in the hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane.

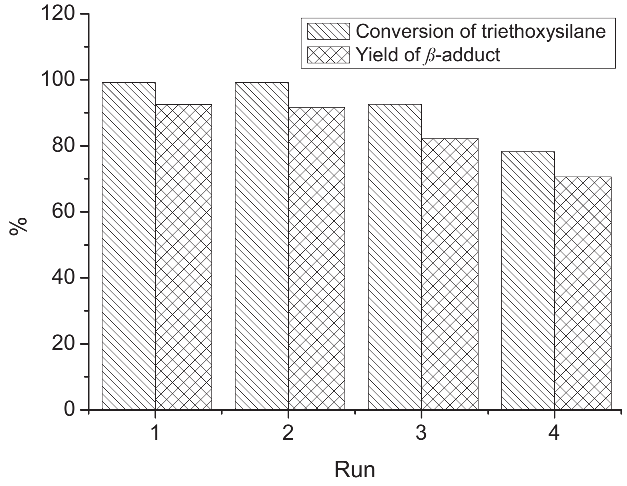


Fig. 3. Catalyst reuse in the hydrosilylation of 3,3,3-trifluoropropene with catalyst 6.

supported Pt-complex. To explore deeper, we think that the bond energy between platinum atom and nitro atom is not strong enough. This point could be inferred from the data of XPS spectra.

3. Conclusions

In this contribution, we have presented a synthetic method for obtaining a novel copolymer of styrene, 2-vinylpyridine, and allyl polyethylene glycol as a cross-linking agent. Furthermore, copolymer-immobilized platinum has been used as a catalyst in the hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane. The presence of 2-vinylpyridine and allyl polyethylene glycol in the polymer was found to increase the yield of adduct. The maximum β-adduct yield of 92.5% was attained at an N/Pt atom ratio of 6:1.

Further studies are aimed at characterizing of catalyst system and investigating the role of polyethylene glycol and ally pyridine for hydrosilylation of 3,3,3-trifluoropropene. Also, mechanical study both in experimental and computational chemistry will be conducted in our following work.

4. Experimental

4.1. Reagents and equipments

Polyethylene glycol (average molecular weight is 200), styrene, allyl-chloride, anhydrous calcium chloride ($CaCl_2$), chloroform, tetrahydrofuran (THF) and platinic chloride ($H_2PtCl_6 \cdot 6H_2O$) were purchased from China National Medicines Corporation Ltd. Sodium hydride (NaH), azodiisobutyronitrile (AIBN) and divinylbenzene were purchased from Alfa Aesar. The monomers styrene and divinylbenzene were washed with sodium hydroxide solution (10% aqueous solution) and water to remove any polymerization inhibitors, then dried with $CaCl_2$ and distilled under reduced pressure. AIBN was recrystallized twice from ethanol.

^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ as solvent. TMS were used as the internal reference for ^1H, ^{13}C and ^{29}Si NMR spectra. $CFCl_3$ was the external reference for ^{19}F NMR spectra. The molecular weights of the polymer were measured by GPC (Waters-1525) in THF solutions with reference to linear polystyrene standards. Elemental analyses of the polymers were obtained on a Vario EL analyzer. X-ray photoelectron spectroscopy (XPS) spectra were performed using a PHI 5000C ESCA System. GC–MS analyses of the hydrosilylation reaction products were obtained with an Agilent 26890N/59731 equipped with a DB-5 column (30 m × 2.5 mm × 0.25 μm).

4.2. Synthesis of APEG 1 (allyl polyethylene glycol)

PEG200 (10.0 g) was dissolved in THF (50 mL) in a three-necked flask, and then NaH (3.6 g) was added portionwise under stirring. The resulting mixture was stirred for 2 h at room temperature. Allyl chloride (16.3 mL) was then added dropwise and the reaction mixture was stirred for 24 h. THF was then removed by distillation under reduced pressure, the crude product was dissolved in chloroform (50 mL), and NaOH was removed by washing with water. The solution was dried over anhydrous magnesium sulfate and filtered to remove the inorganic salt. Finally, the chloroform was evaporated to leave the APEG **1**. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 5.96$–5.87 (m, 2 H, $CHCH_2$), 5.19–5.16 (d, 4 H, $J = 12$, $CHCH_2$), 4.02 (d, 4 H, $J = 4.0$ Hz, OCH_2CH), 3.67–3.59 (br, 16 H, $-OCH_2CH_2O-$).

4.3. General procedure for synthesis of the functional polymers

The typical synthetic method used to obtain the novel polymer is shown in Scheme 3. Styrene (2.1 g) was dissolved in THF (3.0 mL), and then 2,2′-azobisisobutyronitrile (AIBN) and compound **1** were added. The solution was heated to 70 °C and vigorously stirred under exclusion of air. After 20 h, the THF was evaporated at 60 °C in vacuum. The product was redissolved in dichloromethane (5.0 mL) and this solution was dropped into methanol for sedimentation under stirring to obtain polymeric particles. The particles were washed three times each with water and methanol, collected by filtration, and dried at 60 °C in vacuum for 6 h. The components of the polymers were assigned numbers; see Table 1.

4.4. Preparation of the immobilized platinum catalyst

The prepared polymer (P1, P2, P3, P4, P5, P6, P7, P8, or P9, 0.5 g in each case) was suspended in a methanol solution of platinic chloride (5 mL, 0.002 g/mL). The suspension was stirred at room temperature for 48 h or refluxed for 6 h at 60 °C under nitrogen atmosphere. After removing the solvent, the residue was dried at 60 °C in vacuum for 6 h. These catalysts were designated as C1, C2, C3, C4, C5, C6, C7, C8, and C9, respectively.

4.5. Hydrosilylation of 3,3,3-trifluoropropene with triethoxysilane

Catalyst (2.0×10^{-3} mmol Pt) and $(EtO)_3SiH$ (1.07 g, 6.5 mmol) were placed in a 10 mL hermetically sealable vessel with a gas hole. The air in the vessel was replaced with 3,3,3-trifluoropropene through the gas hole three times. The reaction mixture was then stirred at 60 °C for 6 h. The vessel was kept connected to a 3,3,3-trifluoropropene bottle under 0.1 MPa pressure during the course of the reaction. The reaction mixtures were subsequently characterized by GC–MS analysis for conversion of triethoxysilane and yield of adduct. In order to confirm the structure of adduct by NMR, the crude product was purified by a short column chromatography without consideration of the isolated yield. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.88–3.81 (q, 6 H, OCH_2), 2.19–2.07 (m, 2 H, CF_3CH_2), 1.25–1.20 (m, 9 H, CH_3), 0.84–0.80 (m, 2 H, $SiCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 131.63–123.39, 58.30, 28.03, 18.02. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): −69.42. ^{29}Si (80 MHz, $CDCl_3$) δ (ppm): −47.99.

4.6. Catalyst recycling

When the reaction is over, the liquid reactant was shifted out from the reaction vessel after centrifugating for 5 min, and the catalyst leaved in the vessel for next test. The following operation is same to procedure for the hydrosilylation.

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